



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(19)

(11) Publication number:

**0 087 926**  
**A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 83300968.1

(51) Int. Cl.<sup>3</sup>: **G 21 C 21/18**  
**C 04 B 35/10**

(22) Date of filing: 24.02.83

(30) Priority: 26.02.82 US 352731

(43) Date of publication of application:  
07.09.83 Bulletin 83/36

(84) Designated Contracting States:  
DE GB IT SE

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(54) **Burnable neutron absorbers.**

(57) A neutron-absorber body for use in burnable poison rods in a nuclear reactor. The body is composed of a matrix of  $\text{Al}_2\text{O}_3$  containing  $\text{B}_4\text{C}$ , the neutron absorber. Areas of high density polycrystalline  $\text{Al}_2\text{O}_3$  particles are predominantly encircled by pores in some of which there are  $\text{B}_4\text{C}$  particles. This body is produced by initially spray drying a slurry of  $\text{Al}_2\text{O}_3$  powder to which a binder has been added. The powder of agglomerated spheres of the  $\text{Al}_2\text{O}_3$  with the binder are dry mixed with  $\text{B}_4\text{C}$  powder. The mixed powder is formed into a green body by isostatic pressure and the green body is sintered. The sintered body is processed to form the neutron-absorber body. In this case the  $\text{B}_4\text{C}$  particles are separate from the spheres resulting from the spray drying instead of being embedded in the sphere.

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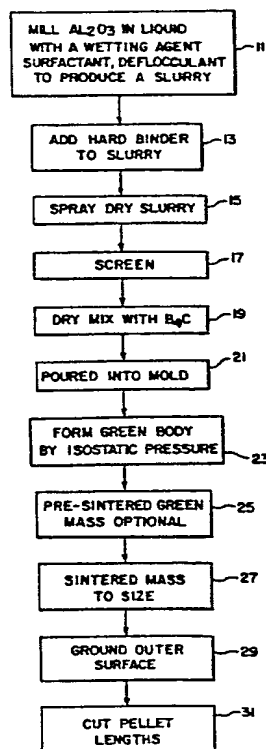


FIG.1.

## BURNABLE NEUTRON ABSORBERS

This invention relates to burnable neutron absorbers, also called burnable poisons, for nuclear reactors. The burnable neutron absorbers with which this invention concerns itself are of the type described in United States patent application Serial No. 352,682 (Radford), filed February 26, 1982. Such neutron absorbers include annular ceramic pellets which are stacked in tubes inserted in the core of a reactor. It is with the pellets that this invention concerns itself. Such a pellet includes a matrix of a refractory material which may include aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or zirconium oxide  $\text{ZrO}_2$  or a combination of the two. A neutron absorber is distributed throughout this matrix. The neutron absorber may include one or more elements or compounds of the metals boron, gadolinium, samarium, cadmium, europium, hafnium, dysprosium and indium. A neutron absorber commonly used is boron carbide ( $\text{B}_4\text{C}$ ) either natural or with the boron enriched  $\text{B}^{10}$ .

In the interest of brevity and concreteness to facilitate the understanding of those skilled in the art in the practice of this invention, this application will deal specifically with a matrix of  $\text{Al}_2\text{O}_3$  and a neutron absorber of  $\text{B}_4\text{C}$ . It is understood that to the extent that this invention is practiced with other materials, such practice is within the scope of equivalents of this invention as scope of equivalents is defined and described in

the Supreme Court Grover case cited in the Radford application.

5 The method of producing pellets disclosed in the above-mentioned Radford application and the pellets produced thereby have proven themselves highly satisfactory. However, experience with this method and the pellets produced thereby has led to the conclusion that several improvements are desirable. It is desirable that the pores or voids in the matrix be more efficiently or effectively used to take up the expansion of the  $B_4C$  and absorb the helium gas generated by the neutron-boron reaction. It is also desirable that the strength, particularly the compressive strength, of the matrix be improved. It is an object of this invention to provide a method for producing  
10 neutron absorbing bodies or ceramics having the above-described desirable properties. It is also an object of this invention to provide a neutron-absorbing body or ceramic having the above desirable properties.

In the procedure of the Radford application, a  
20 slurry of a mixture of  $Al_2O_3$  and  $B_4C$  powder is spray-dried. The resulting dried powder consists of agglomerated spheres of  $Al_2O_3$  in which  $B_4C$  particles are embedded. This powder is then pressed into pellets and sintered. It has been realized in arriving at this invention that the  
25 invention absorbing effectiveness and the resistance to swelling of the ceramic bodies can be improved and at the same time the strength of the ceramic bodies can be increased by separating the  $Al_2O_3$  and the  $B_4C$  in the production of the ceramic bodies.

30 Accordingly, the present invention resides in a method of making a burnable neutron-absorber for the burnable-poison rods of a nuclear reactor characterized by producing a slurry of a powder of a refractory material including one or more of the class consisting of  $Al_2O_3$  and  
35  $ZrO_2$ ; adding a binder to said slurry; drying said slurry to produce a powder of agglomerated particles of aluminum oxide including said binder; mixing said powder with a

powder of the class of neutron-absorber materials consisting of one or more elements or compounds of boron, gadolinium, samarium, cadmium, europium, hafnium, dysprosium and indium, to form a mixture of said powders; isostatically  
5 compressing said mixture to form a green body; sintering said green body to form a sintered body; and forming said sintered body into a neutron absorber of appropriate shape and dimensions.

In carrying out a method according to one embodiment of the invention, a slurry of the  $\text{Al}_2\text{O}_3$  alone is produced. A hard binder, typically polyvinyl alcohol, is added and the slurry and binder are spray dried. The product of the spray drying is a powder of agglomerated  $\text{Al}_2\text{O}_3$  spheres 30 to 50 microns in mean diameter. This  
10 powder is mixed with dry  $\text{B}_4\text{C}$  powder 5 to 15 microns in mean size forming a homogeneous mixture. This mixture is pressed isostatically into green tubes which are then sintered. When the mixture is pressed the agglomerates of  $\text{Al}_2\text{O}_3$  deform and lock together trapping the  $\text{B}_4\text{C}$  particles  
15 in the pores. During sintering, the binder volatilizes and the structure of the resulting ceramic has nearly spherical high-density regions of  $\text{Al}_2\text{O}_3$ . These regions are predominantly surrounded by pores and by  $\text{B}_4\text{C}$  particles.

This results in a preferred location in the  $\text{Al}_2\text{O}_3$  matrix of the  $\text{B}_4\text{C}$  particles and the pores. The matrix of the  $\text{Al}_2\text{O}_3$  consists microscopically of high density polycrystalline regions and its strength is higher than for the matrix produced in the practice of the invention of the Radford application. Since the  $\text{Al}_2\text{O}_3$  is  
20 dried, the hygroscopic tendency of the matrix is materially reduced. The  $\text{B}_4\text{C}$  particles are predominantly in the pores of the matrix. The available porosity accommodates the swelling of the  $\text{B}_4\text{C}$  particles when bombarded by neutrons and the resulting helium gas.  
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In order that the invention can be more clearly understood, a convenient embodiment thereof will now be

described, by way of example, with reference to the accompanying drawings in which:

Fig. 1 is a flow chart of a method of making burnable neutron-absorber ceramic pellets;

5           Fig. 2 is a photomicrograph of a ceramic body produced by the method of Fig. 1; and

Fig. 3 is a photomicrograph of a ceramic body produced in accordance with the method of the above-mentioned Radford application and is presented for comparison purposes.

10           In the first step 11, a powder of  $\text{Al}_2\text{O}_3$  is milled in a ball mill in a liquid, typically water which may be deionized. Small but effective quantities of a wetting agent, a surfactant and a deflocculant are added  
15           to the water and  $\text{Al}_2\text{O}_3$ . The mean size of the  $\text{Al}_2\text{O}_3$  is 10 to 30 microns. The relative quantities of the  $\text{Al}_2\text{O}_3$ , the water and the other components are substantially the same as disclosed in the Radford application. The result of the milling is a slurry containing about 40%  $\text{Al}_2\text{O}_3$  only.

20           In the second step 13 a hard binder, such as polyvinyl alcohol, is added to the slurry. In the third step 15 the slurry is spray dried in apparatus as disclosed in the Radford application. The spray drying results in spheres of agglomerated particles of  $\text{Al}_2\text{O}_3$   
25           having a mean diameter of about 30 to 50 microns. In the fourth step 17 this powder is screened to eliminate excessively large agglomerates. In the next step 19 a homogeneous mixture of the  $\text{Al}_2\text{O}_3$  agglomerates and  $\text{B}_4\text{C}$  powder is produced. The content of the  $\text{B}_4\text{C}$  powder in this mixture  
30           in weight percent may be between 1 and 50. The mean size of the  $\text{B}_4\text{C}$  particles is between 5 and 15 microns.

          The remaining steps 21 to 31 are the same as the corresponding steps of the Radford application. The homogeneous mixture is poured into a mold, step 21. A green  
35           cylinder or green mass is formed by compressing the powder in the mold by isostatic pressure, step 23. Optionally the green cylinder may be presintered, step 25. The mass

is sintered to size, step 27. The sintering is in an atmosphere of argon at about atmospheric pressure and the sintering temperature is between 1400°C and 1800°C. The outer surface of the sintered body is ground, step 29.

5 Ceramic pellets of  $B_4C$  in a matrix of  $Al_2O_3$  are cut from the cylinder.

The microstructure of the ceramic body so produced is shown in Fig. 2. As indicated a length of about 1/16 inch on the photomicrograph corresponds to 5 microns. 10 The black areas 33 on the photomicrograph are reproductions of the pores, the dark-gray areas 35 of the  $B_4C$ . The regions of  $Al_2O_3$  alone are interlocked as appears at 39. The  $B_4C$  regions are in pores surrounding the  $Al_2O_3$  as appears at 41.

15 The photomicrograph shown in Fig. 3 is presented purely for comparison purposes. This photomicrograph also shows black areas 33 corresponding to pores, dark-gray areas 35 corresponding to  $Al_2O_3$  and light-gray areas 37 corresponding to  $B_4C$ . But the interlocked regions of 20  $Al_2O_3$  alone are absent. Nor is the  $B_4C$  in pores encircling the  $Al_2O_3$ . The  $B_4C$  as shown in Fig. 3 intermingles with the  $Al_2O_3$ .

IDENTIFICATION OF REFERENCE NUMERALS USED IN THE DRAWINGS

<u>LEGEND</u>	<u>REF. NO.</u>	<u>FIGURE</u>
MILL $Al_2O_3$ IN LIQUID WITH A WETTING AGENT SURFACTANT, DEFLOCCULANT TO PRODUCE A SLURRY	11	1
ADD HARD BINDER TO SLURRY	13	1
SPRAY DRY SLURRY	15	1
SCREEN	17	1
DRY MIX WITH $B_4C$	19	1
POURED INTO MOLD	21	1
FORM GREEN BODY BY ISOSTATIC PRESSURE	23	1
PRE-SINTERED GREEN MASS OPTIONAL	25	1
SINTERED MASS TO SIZE	27	1
GROUND OUTER SURFACE	29	1
CUT PELLET LENGTHS	31	1



## CLAIMS:

1. A method of making a burnable neutron-absorber for the burnable-poison rods of a nuclear reactor characterized by producing a slurry of a powder of a refractory material including one or more of the class  
5 consisting of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ; adding a binder to said slurry; drying said slurry to produce a powder of agglomerated particles of aluminum oxide including said binder; mixing said powder with a powder of the class of neutron-absorber materials consisting of one or more elements or  
10 compounds of boron, gadolinium, samarium, cadmium, europium, hafnium, dysprosium and indium, to form a mixture of said powders; isostatically compressing said mixture to form a green body; sintering said green body to form a sintered body; and forming said sintered body into a neutron absorber  
15 of appropriate shape and dimensions.
2. A method according to claim 1, characterized in that the mean size of the aluminum oxide powder in the slurry is from 10 to 20 microns and the mean size of the powder of the neutron absorber material is from 5 to 15  
20 microns.
3. A method according to claim 1 or 2, characterized in that the slurry is spray dried producing aluminum oxide spheres of 30 to 50 microns mean diameter.
4. A method according to claim 1, 2 or 3 characterized in that the neutron absorber material in the  
25 mixture of powders is boron carbide ( $\text{B}_4\text{C}$ ) and the content of the  $\text{B}_4\text{C}$  in the mixture in weight percent is from 1 to 50.

5. A method according to any of claims 1 to 4, characterized in that the green body is sintered in an atmosphere of argon at about atmospheric pressure at a temperature of between 1400°C and 1800°C.

5 6. A method according to any of claims 1 to 5, characterized in that the binder is a hard binder.

7. A burnable neutron absorber body for use in the burnable-poison rods of a nuclear reactor, characterized in that said body is formed of a porous matrix of  
10  $\text{Al}_2\text{O}_3$ , said matrix including high-density polycrystalline particles of  $\text{Al}_2\text{O}_3$  juxtaposed to pores in which pores there are particles of  $\text{B}_4\text{C}$ .

8. A body according to claim 7, characterized in that the pores substantially encircle the  $\text{Al}_2\text{O}_3$  particles,  
15 said encircling pores partially or wholly containing particles of  $\text{B}_4\text{C}$ .

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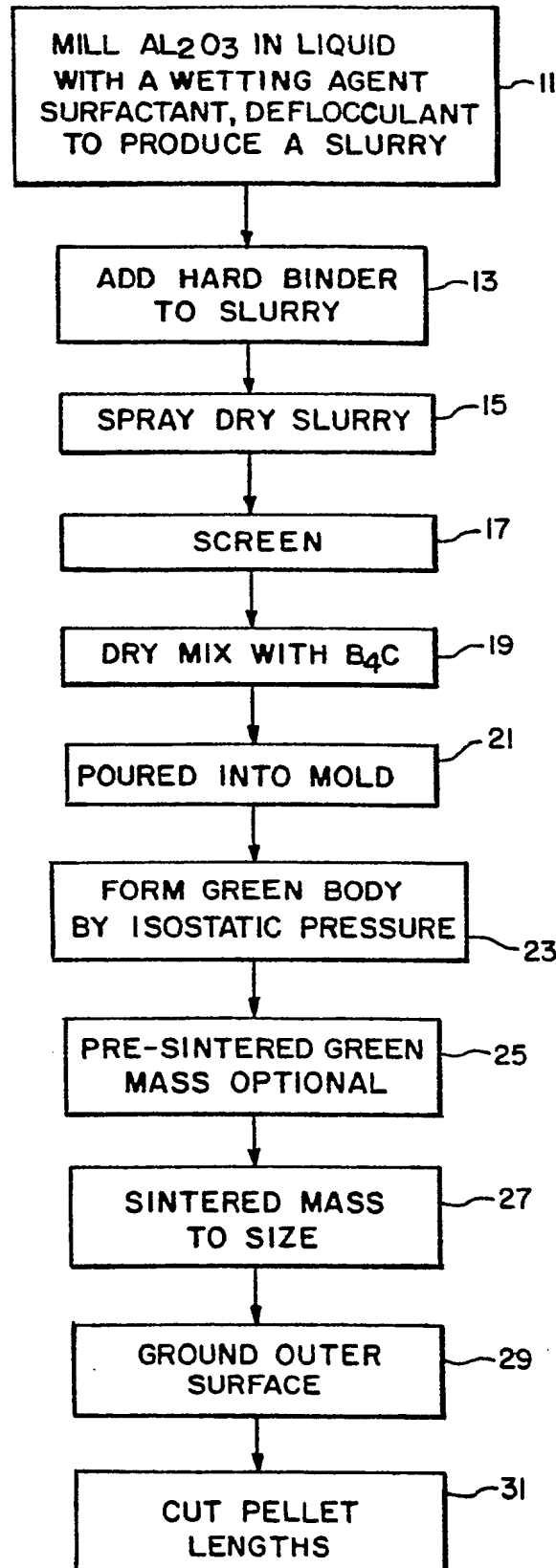


FIG.1.

